

On the long range correlations of thermodynamic systems out of equilibrium

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Experiments show that macroscopic systems in a stationary nonequilibrium state exhibit long range correlations of the local thermodynamic variables. In previous papers we proposed a Hamilton-Jacobi equation for the nonequilibrium free energy as a basic principle of nonequilibrium thermodynamics. We show here how an equation for the two point correlations can be derived from the Hamilton-Jacobi equation for arbitrary transport coefficients for dynamics with both external fields and boundary reservoirs. In contrast with fluctuating hydrodynamics, this approach can be used to derive equations for correlations of any order. Generically, the solutions of the equation for the correlation functions are non-trivial and show that long range correlations are indeed a common feature of nonequilibrium systems. Finally, we establish a criterion to determine whether the local thermodynamic variables are positively or negatively correlated in terms of properties of the transport coefficients.

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The basic idea in the construction of nonequilibrium thermodynamics is that of local equilibrium. This means that on the macroscopic scale it is possible to define local thermodynamic variables like density, temperature, or chemical potentials, which vary smoothly. Microscopically this implies that the system reaches local equilibrium in a time which is short compared to the times typical of macroscopic evolution as described, for example, by hydrodynamic equations. Even if the local behavior of a nonequilibrium system is well described by a Gibbs state, if we probe the system at distances comparable to its macroscopic size, relevant differences with respect to equilibrium do appear. It is indeed an established fact that macroscopic systems in a stationary nonequilibrium state generically exhibit long range correlations of the local thermodynamic variables. For a review of experimental results see [1]. The theories of correlations in thermodynamic systems out of equilibrium that can be found in the literature are mainly based on the so called fluctuating hydrodynamics [2, 3, 4, 5], that is on a linearization around a steady state of the hydrodynamic equations perturbed by random currents. For diluted systems this problem has also been approached within kinetic theory [6].

It has been shown for several stochastic dynamics that the nonequilibrium free energy, which is the generating functional of the correlation functions, satisfies a Hamilton-Jacobi equation [7, 8]. The basic feature of this equation is that it does not depend on the details of the microscopic dynamics but only on the macroscopic transport coefficients, i.e. the diffusion coefficient and the mobility. It can thus be considered as a general principle of nonequilibrium thermodynamics. In this paper

we show how the Hamilton-Jacobi equation can be used to study correlation functions. In contrast with fluctuating hydrodynamics, this approach can be used to derive equations for correlations of any order. For simplicity, we consider diffusive systems in arbitrary dimension described by a single thermodynamical variable with both external fields and boundary reservoirs. We show that the two point function satisfies a linear partial differential equation which depends, as in fluctuating hydrodynamic, on the transport coefficients evaluated in the stationary state. These coefficients can be computed from the microscopic dynamics or can be obtained from experiments. Generically, the solutions of the equation for the correlation functions are non-trivial and show that long range correlations are a common feature of nonequilibrium systems. We remark that the long range correlations arise from nonlinear effects in the hydrodynamic equation. One of the most interesting consequences of the equation for the correlations is that it is possible to establish whether the fluctuations are positively or negatively correlated in terms of structural properties of the transport coefficients.

Systems for which the above scheme can be applied are characterized by a separation of scales both in space and time. We analyze these systems in the limit in which this separation becomes sharp. In the following we let ε be the ratio between microscopic scale, say of order of the intermolecular distance, and the linear size of the system L_0 . Let us consider a macroscopic system in a domain Λ in space dimension d described in terms of a single thermodynamic observable ρ , that we think of as the density of particles. We denote by $\rho(x)$ the local density at the macroscopic point x , obtained as the density of parti-

cles in a volume of side length ℓ , with $\varepsilon L_0 \ll \ell \ll L_0$. We then introduce the corresponding ensemble P_ε as the distribution of such local density. This distribution is inherited from the microscopic ensemble.

According to the Boltzmann–Einstein theory of equilibrium thermodynamic fluctuations [9] the relationship between the free energy F and the probability distribution P_ε is the following

$$P_\varepsilon(\rho(x), x \in \Lambda) \propto e^{-F(\rho)/\varepsilon^d} \quad (1)$$

where we absorbed the temperature T , fixed in the one phase region, in the definition of F . In this equilibrium setting the free energy F is a local functional, i.e. it can be written as

$$F(\rho) = \int_\Lambda dx f(\rho(x)) \quad (2)$$

where $f(\rho)$ is the free energy per unit volume. In particular, there are no correlations, i.e. fluctuations of $\rho(x)$ and $\rho(y)$, for $x \neq y$, are independent.

For systems out of equilibrium, e.g. when they are in contact with reservoirs and/or under the action of an external field E , we let P_ε be the corresponding stationary ensemble. For such systems we define the associated nonequilibrium thermodynamic functional $F(\rho)$ by (1). That this is the appropriate definition is supported by the following facts discussed in [7, 8]. First, the stationary state corresponds to the absolute minimum of F , thus generalizing the maximum entropy principle of equilibrium statistical mechanics. Moreover, the derivative of F with respect to ρ provides the correct definition of thermodynamic force, that is the force responsible for dissipation, as shown in [8].

In order to present the Hamilton-Jacobi equation for the free energy, we introduce the dynamical behavior of the system. The macroscopic evolution of the density is described by a (in general nonlinear) diffusion equation with a transport term corresponding to the external field E , namely

$$\partial_t \rho(t, x) = \partial_i \left[\frac{1}{2} D_{ij}(\rho) \partial_j \rho(t, x) - \chi_{ij}(\rho) E_j(x) \right] \quad (3)$$

where we use Einstein's convention of summing over repeated indices and ∂_i stands for $\partial/\partial x_i$, $i = 1, \dots, d$. In (3) D is the diffusion coefficient and χ is the mobility. This equation has to be supplemented by the appropriate boundary conditions. For nonequilibrium systems in contact with particle reservoirs, this amounts to fix the value of ρ at the boundary of Λ . We denote by $\bar{\rho}(x)$ the stationary density profile, i.e. the unique stationary solution of (3). This is the density profile in which the nonequilibrium free energy F attains its minimum. Equation (3) identifies the current \bar{J} of particles flowing through the system in the stationary profile as

$$\bar{J}_i(x) = - \left[\frac{1}{2} D_{ij}(\bar{\rho}) \partial_j \bar{\rho}(x) - \chi_{ij}(\bar{\rho}) E_j(x) \right] \quad (4)$$

The equation for $\bar{\rho}$ then reads $\partial_i \bar{J}_i(x) = 0$, i.e. \bar{J} is divergenceless.

As shown in [7, 8], the nonequilibrium free energy F is the maximal solution of the Hamilton-Jacobi equation

$$\left\langle \partial_i \frac{\delta F}{\delta \rho}, \frac{1}{2} \chi_{ij}(\rho) \partial_j \frac{\delta F}{\delta \rho} - \frac{1}{2} D_{ij}(\rho) \partial_j \rho + \chi_{ij}(\rho) E_j \right\rangle = 0 \quad (5)$$

where $\langle f, g \rangle = \int_\Lambda dx f(x) g(x)$ and F satisfies the boundary condition $\delta F / \delta \rho|_{\partial \Lambda} = 0$. The derivation of this equation is based on a dynamical argument. One first generalizes the Boltzmann-Einstein formula (1) to space-time trajectories obtaining the asymptotic probability of deviation from solutions of the hydrodynamic equation (3). The functional F can be identified as follows: if at $t = -\infty$ the system is in the stationary profile $\bar{\rho}$ then the probability of observing the profile ρ at $t = 0$ is proportional to $\exp\{-\varepsilon^{-d} F(\rho)\}$. The free energy F solves a variational problem whose associated Hamilton-Jacobi equation is (5). The validity of (5) has been established for stochastic lattice gases for which the local equilibrium can be proven.

In the case of equilibrium systems, in which $E = 0$ and $\rho|_{\partial \Lambda}$ is constant, the profile $\bar{\rho}$ is constant; it is then simple to check that the solution of (5) has the form (2) where the free energy per unit volume $f(\rho)$ satisfies the Einstein relation $D_{ij}(\rho) = \chi_{ij}(\rho) f''(\rho)$, normalized so that $f'(\bar{\rho}) = f(\bar{\rho}) = 0$. For nonequilibrium systems the solutions of (5) cannot, in general, be obtained in a closed form. For special choices of the transport coefficients, which correspond to well studied stochastic dynamics, the solution of (5) can be expressed in terms a non linear boundary value problem, see [8, 10, 11, 12]. Contrary to equilibrium, a general feature of the nonequilibrium free energy F is that it is not a local functional. This implies that macroscopic density correlations do generically appear.

The density-density correlation is defined as

$$C(x, y) \approx \varepsilon^{-d} \int (\rho(x) - \bar{\rho}(x)) (\rho(y) - \bar{\rho}(y)) dP_\varepsilon \quad (6)$$

Note that the scaling ε^{-d} corresponds to the Gaussian fluctuations. This function is related to the non equilibrium free energy F by

$$C^{-1}(x, y) = \frac{\delta^2 F(\rho)}{\delta \rho(x) \delta \rho(y)} \Big|_{\rho=\bar{\rho}} \quad (7)$$

so that $F(\rho) = (1/2) \langle (\rho - \bar{\rho}), C^{-1}(\rho - \bar{\rho}) \rangle + o((\rho - \bar{\rho})^2)$. We next introduce the function $B(x, y)$ by

$$C(x, y) = C_{eq}(\bar{\rho}(x)) \delta(x - y) + B(x, y), \quad x, y \in \Lambda \quad (8)$$

where, as f is the equilibrium free energy per unit volume, $C_{eq}(\rho) = f''(\rho)^{-1}$ gives the (local) equilibrium variance. Notice that, while D and χ are $d \times d$ matrices, C_{eq} , C and B are multiples of the identity. Since the density

fluctuations at the boundary are determined only by the reservoirs, we have that $B(x, y) = 0$ when either x or y is at the boundary of Λ .

In order to write an equation for B , introduce the elliptic differential operator L as

$$L = \frac{1}{2} D_{ij}(\bar{\rho}(x)) \partial_i \partial_j + \chi'_{ij}(\bar{\rho}(x)) E_j(x) \partial_i \quad (9)$$

and $\mathcal{L} = L \oplus L$, i.e. \mathcal{L} satisfies $\mathcal{L}\varphi(x)\psi(y) = \psi(y)L\varphi(x) + \varphi(x)L\psi(y)$. Let finally L^\dagger be the adjoint of L with Dirichlet boundary conditions on Λ , i.e.

$$L^\dagger \varphi(x) = \frac{1}{2} \partial_i \partial_j [D_{ij}(\bar{\rho}(x)) \varphi(x)] - \partial_i [\chi'_{ij}(\bar{\rho}(x)) E_j(x) \varphi(x)]$$

and $\mathcal{L}^\dagger = L^\dagger \oplus L^\dagger$. As shown below, from the Hamilton-Jacobi equation (5) it follows that B satisfies

$$\mathcal{L}^\dagger B(x, y) = -h(x) \delta(x - y) \quad (10)$$

where

$$h(x) = -\partial_i [\chi'_{ij}(\bar{\rho}(x)) D_{jk}^{-1}(\bar{\rho}(x)) \bar{J}_k(x)] \quad (11)$$

The choice of the Dirichlet boundary condition for L corresponds to the vanishing of B at the boundary.

We draw some important consequences of equation (10). Since D is positive definite, \mathcal{L} is an elliptic operator in $\Lambda \times \Lambda$ with Dirichlet boundary condition. Let $G(x, y; x', y')$ be its Green function, i.e. the solution of $-\mathcal{L} G(x, y; x', y') = \delta(x - x') \delta(y - y')$. Then the solution of (10) is

$$B(x, y) = \int_{\Lambda} dz G(z, z; x, y) h(z) \quad (12)$$

Since $G \geq 0$, we conclude that if $h \geq 0$, respectively $h \leq 0$, fluctuations of the density are positively correlated, i.e. $B \geq 0$, respectively negatively correlated, i.e. $B \leq 0$. In absence of external field, i.e. for $E = 0$, we have, from (4) and (11), that $h(x) = \frac{1}{2} \partial_i \partial_j \chi_{ij}(\bar{\rho}(x))$. If we further assume that χ is a multiple of the identity, we get that $B \geq 0$, respectively $B \leq 0$, if $\chi(\bar{\rho}(x))$ is a subharmonic, respectively superharmonic, function of x , namely $\Delta \chi(\bar{\rho}(x))$ is positive, respectively negative.

For equilibrium systems the current \bar{J} in the stationary profile vanishes, hence $h = 0$ so that $C = C_{eq}$. This conclusion is also true for systems with periodic boundary conditions and constant external field. In such case $\bar{\rho}$ and \bar{J} are constant so that h vanishes. More generally, in [13] it is shown that, in the periodic case, the nonequilibrium free energy F is the same as the equilibrium one. For isotropic systems D and χ are multiples of the identity, in such a case h vanishes if and only if $\partial_i [\chi'(\bar{\rho}(x)) D^{-1}(\bar{\rho}(x))] \bar{J}_i(x) = 0$ for any x in Λ . For instance, in the zero range process χ is an increasing function and $D = \chi'$, so that h vanishes and the model does not exhibit long range correlations.

We now consider some one-dimensional systems and choose $\Lambda = (0, 1)$. We let $\rho(0) = \rho_0 \leq \rho_1 = \rho(1)$ be the boundary conditions imposed by the reservoirs. The one-dimensional exclusion process has $0 \leq \rho \leq 1$, $D(\rho) = 1$, $\chi(\rho) = \rho(1 - \rho)$. For $E = 0$ equation (10) implies that B is proportional to the Green function of the Dirichlet Laplacian in $(0, 1)$, namely

$$B(x, y) = -(\rho_1 - \rho_0)^2 x(1 - y), \quad 0 \leq x \leq y \leq 1 \quad (13)$$

This result was first derived in [3]. Notice that, in agreement with the above discussion, since χ is concave and $\bar{\rho}'$ is constant, $B \leq 0$. For constant external field E the solution of (10) is given by

$$B(x, y) = 2\bar{J} \bar{\rho}'(x) \bar{\rho}'(y) \frac{\int_0^x du \bar{\rho}'(u)^{-1} \int_y^1 du \bar{\rho}'(u)^{-1}}{\int_0^1 du \bar{\rho}'(u)^{-1}} \quad (14)$$

for $0 \leq x \leq y \leq 1$. This formula for the correlation function has been derived in [14]. It can be shown that $\bar{\rho}$ is increasing. Therefore the correlations $B(x, y)$ have the same sign as \bar{J} . We finally discuss the correlations in the Kipnis-Marchioro-Presutti model [11, 15]. This model describes a chain of one-dimensional harmonic oscillators which are mechanically uncoupled and interact by exchanging stochastically the energy with the neighboring sites. Accordingly, the thermodynamic variable ρ is the energy density. For this model $D(\rho) = 1$ and $\chi(\rho) = \rho^2$. The solution of (10) is then the same as the one for the exclusion model, i.e. (13), but with the opposite sign. For this model the energy fluctuations are therefore positively correlated, in agreement with the above discussion and the fact that χ is a convex function. Since B is proportional to Green function of the Dirichlet Laplacian, we also have that it is a positive definite operator. This means that, in the quadratic approximation near $\bar{\rho}$, the nonequilibrium free energy is smaller than the local equilibrium one. The opposite behavior takes place in the exclusion process. For these models this result has been proven also for large fluctuations, that is beyond the quadratic approximation [8, 10, 11].

We here show that the above results can be seen as special cases of a class of one-dimensional systems for which (10) can be solved explicitly. Assume that

$$2\chi'(\bar{\rho}(x)) E(x) h(x) = \partial_x [D(\bar{\rho}(x)) h(x)] \quad (15)$$

holds for any x in $(0, 1)$. Then it is simple to check that the operator $\hat{L} = -2h(x)^{-1} L^\dagger$ is self-adjoint and B is its Green function. By standard Sturm Liouville theory we then get

$$B(x, y) = \frac{1}{K} \alpha_1(x) \alpha_2(y), \quad 0 \leq x \leq y \leq 1 \quad (16)$$

where α_i , $i = 1, 2$, solves the Cauchy problem $\hat{L} \alpha_i = 0$, with $\alpha_1(0) = 0$, $\alpha_1'(0) = 1$ and $\alpha_2(1) = 0$, $\alpha_2'(1) = 1$.

Finally $K = -[D(\bar{\rho}(x))/h(x)]W(\alpha_1, \alpha_2)$, where W is the Wronskian, is constant in x . Both for the exclusion and the KMP processes (15) holds for any constant external field E . Simple computations then yield (13) and (14) as special cases of (16). Moreover, from (16) we also get the correlation function $B(x, y)$ for the KMP model with constant external field, which is the same as (14) with opposite sign.

To conclude we show how equation (10) can be derived from the Hamilton-Jacobi equation for the nonequilibrium free energy. To derive the equation for the correlations, it is convenient to introduce $G(\lambda)$ as the Legendre transform of $F(\rho)$, i.e. $G(\lambda) = \sup_{\rho} \{ \langle \lambda, \rho \rangle - F(\rho) \}$. The function $\lambda(x)$, x in Λ , can be interpreted as the variation of the chemical potential, in particular $\lambda = 0$ corresponds to the stationary profile $\bar{\rho}$. By Legendre duality, equation (5) is then equivalent to

$$\frac{1}{2} \left\langle \partial_i \lambda, \chi_{ij} \left(\frac{\delta G}{\delta \lambda} \right) \partial_j \lambda \right\rangle - \left\langle \partial_i \lambda, \frac{1}{2} D_{ij} \left(\frac{\delta G}{\delta \lambda} \right) \partial_j \frac{\delta G}{\delta \lambda} - \chi_{ij} \left(\frac{\delta G}{\delta \lambda} \right) E_j \right\rangle = 0$$

for any λ which vanishes at the boundary of Λ . In the quadratic approximation we have $G(\lambda) = \langle \lambda, \bar{\rho} \rangle + (1/2) \langle \lambda, C \lambda \rangle + o(\lambda^2)$. Since $\bar{\rho}$ is the stationary solution of (3), the first order term in λ vanishes in the above equation, so that C solves

$$\left\langle \partial_i \lambda, \frac{1}{2} \chi_{ij}(\bar{\rho}) \partial_j \lambda - \frac{1}{2} \partial_j (D_{ij}(\bar{\rho}) C \lambda) + \chi'_{ij}(\bar{\rho}) E_j C \lambda \right\rangle = 0$$

By plugging (8) in the above equation, recalling (4) and $D_{ik}^{-1}(\bar{\rho}) \chi_{kj}(\bar{\rho}) = C_{eq}(\bar{\rho}) \delta_{ij}$, we get

$$\begin{aligned} & \left\langle \partial_i \lambda, -\frac{1}{2} \partial_j (D_{ij}(\bar{\rho}) B \lambda) + \chi'_{ij}(\bar{\rho}) E_j B \lambda \right\rangle \\ &= - \left\langle \partial_i \lambda, \chi'_{ij}(\bar{\rho}) D_{jk}^{-1}(\bar{\rho}) \bar{J}_k \lambda \right\rangle \end{aligned}$$

Integrating by parts we then get

$$\begin{aligned} & \left\langle \lambda, \frac{1}{2} \partial_i \partial_j (D_{ij}(\bar{\rho}) B \lambda) - \partial_i (\chi'_{ij}(\bar{\rho}) E_j B \lambda) \right\rangle \\ &= \frac{1}{2} \left\langle \lambda, \left[\partial_i (\chi'_{ij}(\bar{\rho}) D_{jk}^{-1} \bar{J}_k) \right] \lambda \right\rangle \end{aligned}$$

Recalling (9) and (11), the above equation can be written in an operator notation as

$$L^\dagger B + B L = -h$$

Here h denotes a multiplication operator and we used that $B(x, y) = B(y, x)$. Denote by L_x^\dagger , respectively L_y^\dagger , the operator L^\dagger acting on functions of x , respectively of y . From the previous equation we get that for any function φ vanishing on $\partial\Lambda$ we have

$$\int_{\Lambda} dy \left[L_x^\dagger B(x, y) \varphi(y) + L_y^\dagger B(x, y) \varphi(y) \right] = -h(x) \varphi(x)$$

that is (10).

We conclude with some comments on the applicability of equation (10). The Hamilton-Jacobi equation from which it is derived was originally introduced in the study of microscopic models whose macroscopic behavior is of diffusive type and there are no normal modes like sound waves. This case covers for example nonequilibrium solutions of different chemical species but no chemical reactions. The Hamilton-Jacobi equation is strictly connected with the dynamic generalization of the Einstein formula for static fluctuations obtained in [7, 8] and it has been extended to systems without conservation laws [13, 16] where the hydrodynamic equations are of reaction-diffusion type, as it happens in presence of chemical reactions. It can be generalized to situations with several conservation laws where one of the hydrodynamic equations is Navier-Stokes. We finally emphasize that the approach here presented, based on an exact equation for the nonequilibrium free energy which takes into account the nonlinear effects in the systems, can be applied to derive equations for higher order correlations.

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